



Study of potassium-supported TiO₂ catalysts for the production of biodiesel

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ARTICLE INFO

Article history:

Received 17 October 2011

Received in revised form

22 December 2011

Accepted 17 January 2012

Available online 30 January 2012

Keywords:

Heterogeneous transesterification

Biodiesel

Canola oil

Potassium

TiO₂

ABSTRACT

A hydrotreated TiO₂ supported potassium catalyst, K/TiHT, was studied on the transesterification reaction of canola oil for the production of biodiesel. It was found that the calcination at different temperatures led to the transformation of the supported potassium catalyst into a titanate form of oxide. This was accompanied by a substantial increase in activity. Leaching studies found that although some potassium and titania was left in the products, the reaction mainly occurred in heterogeneous conditions. The contribution of the leached components to the activity was only minor. The recovered catalyst was then used in successive reactions producing stable conversions. A maximum conversion was achieved with the catalyst calcined at 700 °C. Optimum reaction conditions were obtained when using a catalyst loading of 6% (w/w), a methanol to oil ratio of 54:1, and a temperature of reaction of 55 °C.

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1. Introduction

During the last decades, the increasing global demand for energy sources, traditionally based in fossil fuels, and the concern for environmental protection have encouraged research in renewable energy alternatives. Because of this, biodiesel derived from the transesterification of vegetable oils or animal fats has gained considerable attention. This fuel is biodegradable and its similarity with conventional diesel (energy content, cetane number, viscosity) makes it usable in existing diesel engines. In addition, biodiesel has very low amounts of sulfur and its combustion emits much lower particulates, unburned hydrocarbons, and lower amounts of carbon monoxide than petroleum-based diesel fuel. In the transesterification reaction, the oil is mixed with an alcohol, commonly methanol, and with a catalyst, traditionally NaOH and KOH, producing methyl esters (biodiesel) and glycerol. However, this homogeneous route has several drawbacks such as high purification costs of the obtained biodiesel, the generation of large amounts of wastewater, and the impossibility of reusing the catalyst. As an alternative to overcome these issues, extensive research has been done on solid bases [1]. The use of solids on the heterogeneous transesterification of oils results in much purer products, which in turn drastically reduce the use of water needed to remove the alkali from the biodiesel, since the solid catalyst can be easily recovered from the liquid product. Therefore, this not only reduces

the amount of wastewater but, it is also possible to reuse the solid catalyst.

A variety of materials are extensively reported in literature and applied to the heterogeneous transesterification of oils [1,2]. In particular, potassium supported catalysts have shown to be an active material in the production of biodiesel. Among others, the commonly used supports in potassium supported catalysts are Al₂O₃ [3–11], aluminosilicates [12,13], metal oxides [3,14,15], zeolites [16,17], clays [18], hidrotalcites [19,20], and activated carbon [21,22]. The selection of the potassium precursors also vary within the literature of which the most common is the use of KOH [6,9,11,16–18,21,22], KF [3,4,9,15,20], KNO₃ [7,8,10,14], KI [9,23], and K₂CO₃ [5,9,12,13]. The literature shows that the reaction conditions that are usually studied, such as methanol to oil molar ratio, reaction temperature, and catalyst loading, are strongly dependent on the type of support and potassium precursor. Among the most active potassium supported catalysts is that of Martín-Alonso et al. [5], who by using a K/γ-Al₂O₃ catalyst reported full conversion to methyl esters with the following conditions: the use of a methanol to oil ratio of 25:1, a catalyst loading of 2.8% (w/w), a reaction temperature of 60 °C, and a 1 h of reaction time. In this case, the transesterification reaction was carried out under an inert atmosphere of nitrogen. A similar conversion was achieved by Lukić et al. [12] on a K₂CO₃/Al₂O₃-SiO₂ catalyst using a pressurized reaction system. He used a methanol to oil ratio of 15:1, catalyst loading of 2% (w/w), reaction temperature of 120 °C, and about 1 h of reaction time. Furthermore, several other studies have demonstrated that the use of ambient pressure and mild temperatures (lower than 70 °C) are able to lead to methyl ester conversions higher than 95%

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[3,4,9,20,22,24]. Moreover, in our previous report [25], we demonstrate that when potassium nitrate is supported on a hydrotreated TiO₂ support, we obtained a highly active catalyst, which was able to achieve full conversion to methyl esters after 5 h of reaction time. The transesterification reaction was carried out at 65 °C, with a methanol to oil molar ratio of 36:1, and a catalyst loading of 6% (w/w).

In this present work, the heterogeneous TiO₂-based potassium supported catalyst is studied in detail in relation to the transesterification of canola oil in contact with air, which to date and apart from our previous report [25], has not been explored. Here, we report the strong effects of the catalyst structure on the final transesterification activity. We also study the different reaction conditions required to optimize the transesterification reaction, such as the effect of the ex situ calcination temperature of the catalyst before the reaction, the amount of catalyst loaded into the reactor, the methanol to oil molar ratio, and the reaction temperature. Since one of the most important and practical characteristics of these materials is the potential to reuse the spent catalysts, we report the transesterification activity after consecutive runs and study the effect of the alkali leaching on the observed activities.

2. Experimental

A set of catalysts were prepared by subjecting the TiO₂ (150 m²/g, Aldrich) to a hydrothermal treatment [26,27]. In brief, 2 g of TiO₂ were heated in a 10 M solution of NaOH at 110 °C for 24 h and then put in contact with a 0.1 M solution of HCl overnight at room temperature. The filtered solid was then washed and dried. The obtained support, denoted TiHT, had a BET area of 286 m²/g. The TiHT support was dry-impregnated with 20% (w/w) potassium using KNO₃ (Merck) as a precursor. The impregnated catalysts were then calcined in air at 500 °C for 3 h. The final catalysts were denoted as x%K/TiHT, where x corresponds to the loading of K.

The transesterification reaction of commercial grade edible canola oil was carried out in a glass batch reactor under reflux and stirring at 65 °C. No inert atmosphere was used and all reactions occurred in contact with air and at ambient pressure. The solid catalyst corresponded to 6% (w/w) of the loaded oil and a molar ratio of oil to methanol of 1:36 was used, unless otherwise noted (20 g of canola oil, 23.1 g of methanol, and 1.2 g of catalyst). The methanol used (Merck) was GC grade (99.9%) with less than 0.05% water. To monitor the evolution of the reaction, a small aliquot was analyzed by a chromatograph with the following sampling procedure: 0.5 ml of the sample was injected into a vial containing 0.5 ml of 0.1 M HCl to stop the reaction. Then, 0.5 ml of the extracting solution was added to the same vial. The extracting solution consisted of hexane:diethylether (1:1) which contained a reference standard (eicosane, 5000 ppm). The vial was then stirred and centrifuged to separate the different phases. A small aliquot from the top phase, which contained the methyl esters, was injected into the chromatograph. The chromatograph (PerkinElmer, Autosystem) was equipped with an Omegawax 250 capillary column (30 m × 0.25 mm × 0.25 μm) (Supelco) and FID detector.

The surface area (BET) and pore size distribution of all samples were obtained by N₂ adsorption using a Micromeritics sorptometer adsorption apparatus (Model ASAP 2010). Before measuring the area, all samples were properly degasified at 200 °C. The crystal structure of the different catalysts was determined by X-ray diffraction, which was carried out on a Siemens D-5000 diffractometer using Cu K_α radiation at a scan rate of 0.02°/min. Thermal gravimetric analysis (TGA) was carried out in a Mettler Toledo (TGA/SDTA 851E) using a carrier of N₂ at a flow of 60 cm³/min. A heating rate of 20°/min from 25 °C up to 900 °C was used. Diffuse reflectance

Table 1

BET area and pore volume of the 20%K/TiHT catalyst calcined at different temperatures.

Calcination temperature (°C)	BET area (m ² /g)	Pore volume (cm ³ /g)
300	18	0.13
400	28	0.24
500	19	0.16
600	11	0.06
700	2	0.02

infrared (DRIFTS) experiments were done in a Vector 22 (Bruker) equipped with a diffuse reflectance cell (Harrick Scientific). Before DRIFTS analysis, all the samples were in situ heated at 200 °C for 1 h. Then CO₂ was flown through the DRIFTS cell for 1 h at 200 °C and the spectra were recorded.

Raman spectroscopy was performed in a Renishaw Microscope System RM1000 using an Argon ion laser as an illumination source (514.5 nm) and an electrically cooled CCD detector. The Raman equipment was coupled to a LECA microscope (50× magnifications) with a collection optic used in backscattering configuration. The laser power was kept in a range of 1.0–3.0 mW to prevent heating the sample. Inductive coupled plasma optical emission spectroscopy (ICP-OES) was carried out on a PerkinElmer Optima 7300 V optical emission spectrometer equipped with a segmented-array charge couple device (SCD) as a detector. Before analysis, a sample aliquot was diluted several times in a nitric acid solution. The results were contrasted against the standards of each analyzed element. The ICP analysis of each sample was carried out several times to ensure reproducibility of the results.

3. Results

In our previous work we found that K/TiHT catalysts were active in the transesterification of canola oil to methyl esters [25]. We also found that the most active catalyst was one with a 20% potassium loading. Consequently, the 20%K/TiHT catalyst is studied here in detail under different reaction conditions and pretreatments of the catalysts.

3.1. BET surface area measurements

As we will show below, the specific calcination temperature of the 20%K/TiHT catalyst resulted in distinctive spectroscopic patterns and activity performances. Because of this, the BET area and pore volume were both determined for selected calcination temperatures for the 20%K/TiHT catalyst. The results are shown in Table 1, where it can be observed that the hydrothermally treated support had a BET area of 286 m²/g, which is a rather different behavior than that observed on the impregnated catalysts. The calcination of the 20%K/TiHT catalyst at 300 °C and 400 °C gave BET areas of 18 and 28 m²/g, respectively. As we will show, the lower BET area from the calcination at 300 °C is due to only partially removing the remaining nitrates from the impregnation of the potassium precursor. This effect is partly eliminated by calcining at 400 °C, which results in a higher BET area, but as shown below, nitrates still remain on the support. A similar effect is observed on the pore volumes of the samples calcined at 300 °C and 400 °C, which show values of 0.13 and 0.24 cm³/g, respectively. On the other hand, the calcination at 500 °C, 600 °C, and 700 °C, led to a gradual decrease of both the BET area and the pore volume with values of 19, 11 and 2 m²/g and 0.16, 0.06 and 0.02 cm³/g, respectively. Such small values for the areas at the higher calcination temperatures were previously ascribed to the deposition of potassium, which gradually fills pores [25]. As shown below, some remaining potassium nitrate is still present up to 500 °C and only completely disappears when calcining above 600 °C. The calcination at

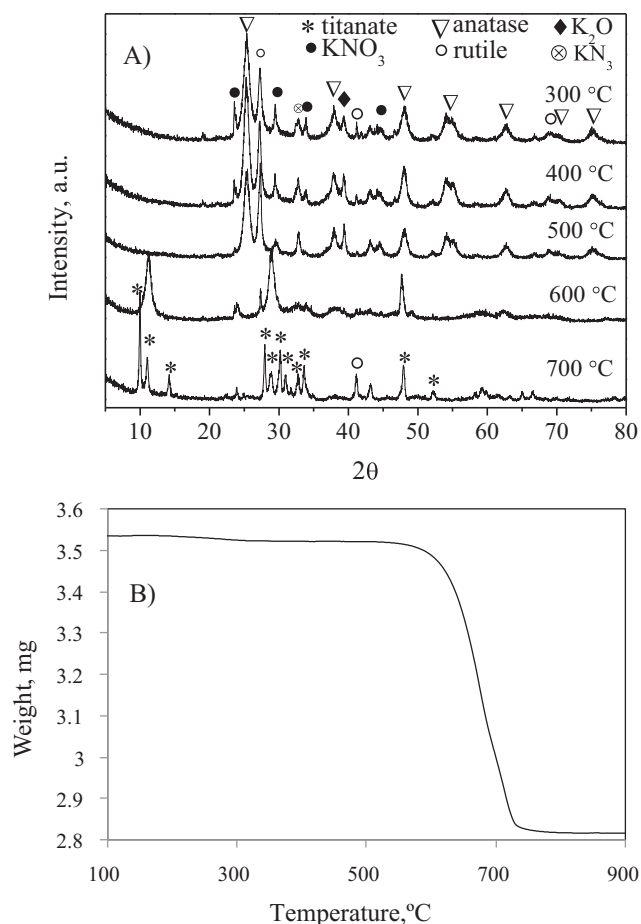


Fig. 1. (A) X-ray diffraction spectra of the 20%K/TiHT catalyst calcined before reaction at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C. Each curve is correspondingly labeled with the calcination temperature. The crystalline phases are also correspondingly labeled as titanate (JCPDS N° 00-032-0861 and 00-041-1100), anatase (JCPDS N° 01-086-1156), KNO_3 (JCPDS N° 00-005-0377), rutile (JCPDS N° 01-089-0552), K_2O (JCPDS N° 00-23-0493), and KN_3 (JCPDS N° 01-073-2426). (B) Thermal gravimetric analysis of the 20%K/TiHT catalyst pre-calcined at 500 °C. A flow of $60 \text{ cm}^3/\text{min}$ of N_2 and a heating rate of $20^\circ/\text{min}$ from 25°C up to 900°C were used.

temperatures above 600°C seems to affect the crystalline structure of the catalyst as shown below, which leads to an abrupt decrease of the BET area and the pore volume.

3.2. X-ray diffraction and thermal gravimetric analysis

In order to understand the effect of the calcination temperature on the transesterification activity, the catalysts were calcined at different temperatures and their crystalline structures analyzed using X-ray diffraction (XRD). Fig. 1A shows the resulting XRD spectra after calcining the 20%K/TiHT catalyst at 300°C , 400°C , 500°C , 600°C , and 700°C . It can be observed that the spectra of the samples calcined at 300°C , 400°C , and 500°C are very similar. The main crystalline structure of these samples corresponds to the anatase phase of the TiO_2 support with a small contribution of rutile. The presence of diffraction lines from KNO_3 indicates that part of the potassium precursor was trapped inside the pores of the support [25]. It can be observed that the signal from K_2O is clearly more intense on the samples calcined at 400°C and 500°C .

When calcined at 600°C the resulting spectrum greatly differs from those previously described and is even more accentuated when calcination occurs at 700°C . Although a small signal from the rutile phase is observed on the sample calcined at 700°C , the main features correspond to a potassium titanate phase [28]. It is clear

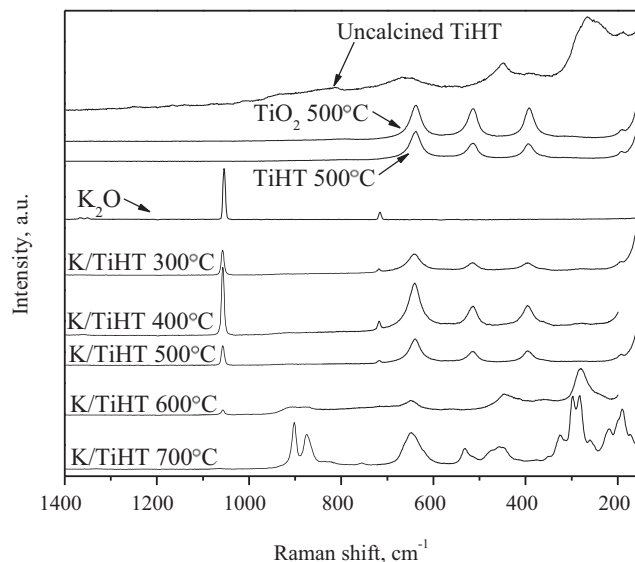


Fig. 2. Raman shift corresponding to (from the top): uncalcined TiHT, TiO_2 calcined at 500°C , TiHT calcined at 500°C , K_2O , 20%K/TiHT calcined at 300°C , 400°C , 500°C , 600°C , and 700°C . Each curve is correspondingly labeled in the same order from top to bottom.

that the calcination at temperatures higher than 500°C induces an abrupt change on the crystalline structure of the TiHT support. In fact, the TGA spectrum of Fig. 1B shows that an abrupt weight loss occurs in the $570\text{--}720^\circ\text{C}$ region, which can be ascribed to either the transformation into potassium titanate or the decomposition of potassium carbonates from the catalyst surface. However, reported results indicate that the decomposition of potassium carbonates occurs around 900°C in flowing N_2 [29]. Therefore, we ascribed the observed weight loss, centered at 670°C , to the phase transformation from anatase to potassium titanate, which might be due to the loss of structural water [30].

3.3. Raman spectroscopy

In order to obtain more detailed information on the crystalline structure of the catalysts, Raman spectra were recorded on the calcined supports and catalysts. The results in Fig. 2 show that the uncalcined TiHT support had broad peaks located at 266 cm^{-1} , 450 cm^{-1} , and 668 cm^{-1} . In comparison, both calcined TiO_2 and TiHT supports (second and third curves from the top) had similar spectra, with three distinctive peaks at 395 cm^{-1} , 515 cm^{-1} , and 638 cm^{-1} , which are characteristic of the anatase phase [31]. The differences between the spectra of the uncalcined TiHT and the supports that are in full anatase are attributed to the structural changes of the TiO_2 support due to the hydrotreatment step during preparation. Such treatment induces a change from three-dimensional crystallites into sheets of TiO_2 [32]. The latter structure is unstable and collapses to anatase after being calcined (third curve from the top) [33]. Fig. 2 shows that the calcination of the 20% K/TiHT catalyst at 300°C , 400°C , and 500°C led to similar spectra with the anatase phase clearly observed in both samples. An additional feature appeared at 1058 cm^{-1} in the K/TiHT catalyst corresponding to the potassium oxide (reference spectrum also included in Fig. 2). In comparison with the previous calcination temperatures the spectrum of the K/TiHT catalyst calcined at 600°C , showed the disappearance of the anatase peaks and the appearance of new features around 280 cm^{-1} , 445 cm^{-1} , and 900 cm^{-1} . The latter peaks are more defined on the sample calcined at 700°C , which would correspond to the characteristic spectra of potassium titanate [34–37]. These results, as well as

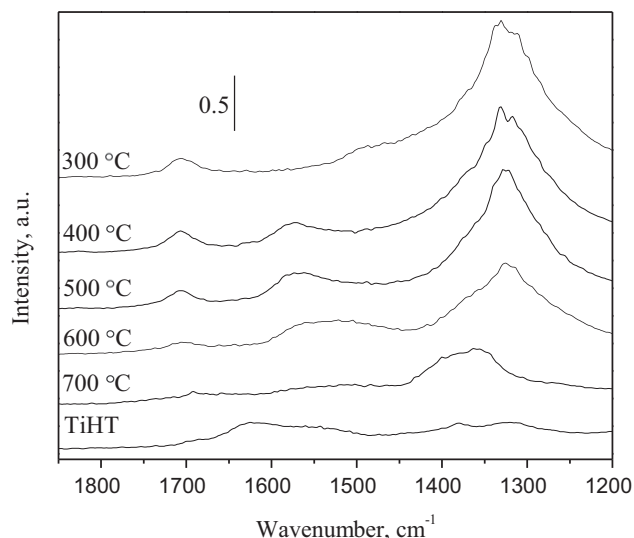


Fig. 3. Diffuse reflection infrared spectra of 20%K/TiHT catalyst calcined before reaction at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C. The TiHT support is also included as a reference. The spectra were recorded after 1 h of running CO₂ at 200 °C.

those from XRD, clearly show that calcination temperatures higher than 500 °C induce a rearrangement of the crystalline structure resulting in the formation of a potassium titanate structure of the catalyst.

3.4. Diffuse reflectance infrared spectroscopy

It is well known that CO₂ can be adsorbed on hydroxylated surfaces, forming a variety of species [38] and references therein). This property of CO₂ makes it a suitable probe for a qualitative, indirect, measurement of the basicity of the surface. Therefore, in order to correlate the basic strength of the catalysts with the calcination temperature we performed CO₂ adsorption and recorded the diffuse reflectance spectra for each catalyst. The results are depicted in Fig. 3, which shows that the formation of carbonates at 1710 cm⁻¹ and 1570 cm⁻¹, bicarbonates at 1430 cm⁻¹, and formates at 1300–1400 cm⁻¹ [39] were observed for the samples calcined between 300–600 °C. The intensity of formates at low frequencies on the sample calcined at 700 °C decreased, indicating a possible change in both the amount and intensity of basic sites of this catalyst. The TiHT support, also included as a reference in Fig. 3, did not show important adsorption of CO₂.

3.5. Effect of the calcination temperature on the transesterification activity

The effect of the calcination temperature on the activity was studied by calcining the 20%K/TiHT catalyst at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C. This calcination step was carried out ex situ, and thereafter the catalysts were exposed to air before reaction. No other in situ treatment was done on the catalyst previous to the reactions, which were carried out in contact with the air. Fig. 4A shows that when the catalyst was calcined at 300 °C the conversion to methyl esters was always lower than 30% and activity did not increase with time; possibly due to deactivation of the active sites. On the other hand, calcining the 20%K/TiHT catalyst at 400 °C resulted in much higher activity with almost full conversion to methyl esters after 7 h of reaction. Increasing the calcination temperature to 500 °C gave higher conversion to methyl esters than before, especially at lower reaction times. An abrupt increase in the conversion activity to methyl ester was observed when increasing the calcination temperature of the catalysts to 600 °C and 700 °C,

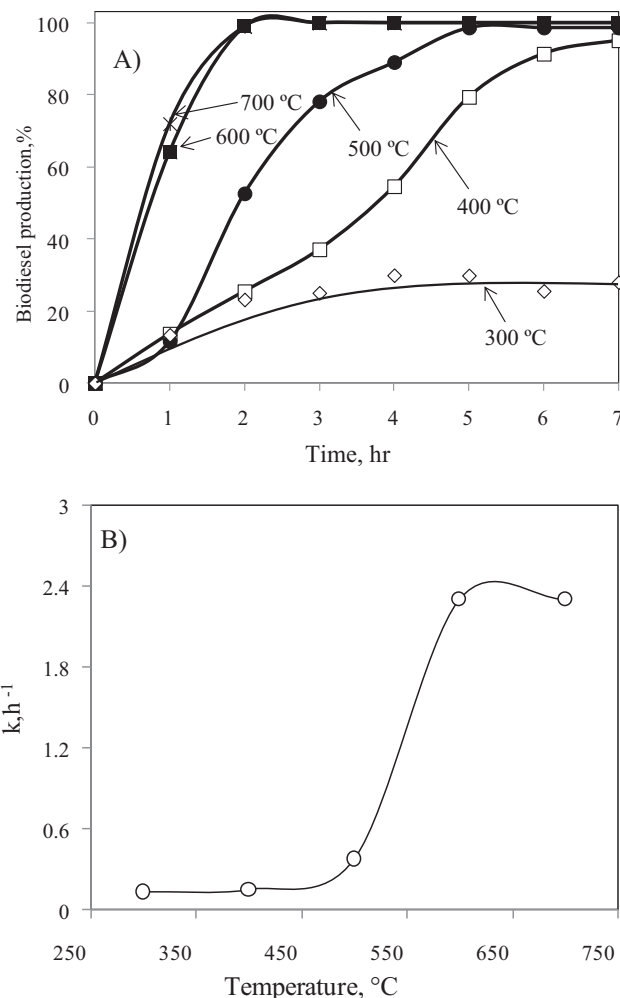


Fig. 4. Transesterification reaction with the 20%K/TiHT catalyst calcined at 300 °C, 400 °C, 500 °C, 600 °C, and 700 °C. (A) Conversion to methyl esters with time (each curve is correspondingly labeled with the calcination temperature of the catalyst), and (B) variation of the constant rate with the calcination temperature of the 20%K/TiHT catalyst after 2 h of reaction. No inert environment was used during the reaction. Reaction conditions: catalyst loading of 6% (w/w), methanol to oil ratio of 36:1, and reaction temperature at 65 °C.

Fig. 4A. The experimental results of the transesterification reaction were fitted to a first-order rate law, Fig. 4B, which clearly shows a noticeable increase in the constant rate above the calcination temperature of 500 °C.

3.6. Variables of reaction

In order to monitor the performance of the 20%K/TiHT catalyst with different variables of reaction, several factors were studied such as the effect of the catalyst loading, the methanol to oil ratio, the temperature of reaction, and the reusability of the catalyst after several consecutive runs. Since the lowest calcination temperature to obtain a catalyst able to reach full conversion to biodiesel was 500 °C, the following studies were carried out with the 20%K/TiO₂ catalyst calcined at 500 °C.

3.6.1. Effect of catalyst loading

The effects of catalyst mass were studied by varying the amount of catalyst loaded into the reactor in respect to the mass of oil used in the reaction. Fig. 5A shows the conversion of methyl ester over time using different weight percentages of catalyst. These experimental results were fitted to a first-order rate law in which the

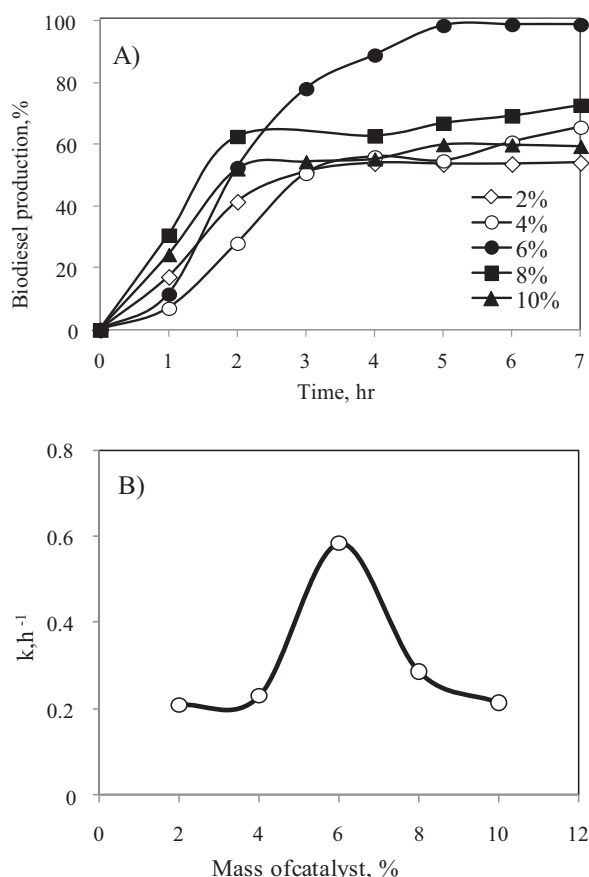


Fig. 5. Conversion to methyl esters with time of reaction on the 20%K/TiHT catalysts: (A) effect of the amount of catalyst on the activity of transesterification, and (B) transesterification rate fitted to a first order kinetics (first 3 h). The labeled percentages correspond to the fraction of solid catalyst (weight%) in respect to the oil in the reaction. The reaction was carried out in contact with air. All catalysts were calcined at 500 °C. The methanol to oil ratio used was of 36:1.

rate constant was plotted in Fig. 5B. Fig. 5A and B shows that the rate increases with the mass of catalyst up to a maximum of 6% and then decreases with any higher loadings. The loadings of 8% and 10% created catalyst accumulation on the wall of the glass reactor, possibly contributing to diffusional problems during reaction and, therefore, lowering the activity.

3.6.2. Effect of the methanol to oil molar ratio

The effect of increasing the methanol to oil molar ratio was also studied with the 20%K/TiHT catalysts. Fig. 6A shows the methyl ester conversion over time using molar ratios of methanol to oil of 6:1, 12:1, 18:1, 27:1, 36:1, 54:1, and 72:1. The lower methanol to oil ratios resulted in poor suspension of the slurry in the reacting solution, which possibly induced mass transfer problems thus resulting in lower activity [40]. On the other hand and in accordance with reported literature, the activity steadily increased with higher methanol to oil ratios. The latter fact is reflected in Fig. 5B, which clearly shows that the constant rate gradually increases with the methanol to oil ratio. During reaction, it is clear that higher amounts of methanol facilitate the suspension of the solid catalysts which might be contributing to the elimination of mass transfer problems.

3.6.3. Effect of the temperature of reaction

The effect of the reaction temperature was studied by conducting the transesterification reaction at room temperature (25 °C), 40 °C, 55 °C, and 65 °C. The reaction temperatures were limited to a range in which the condensation of methanol could be

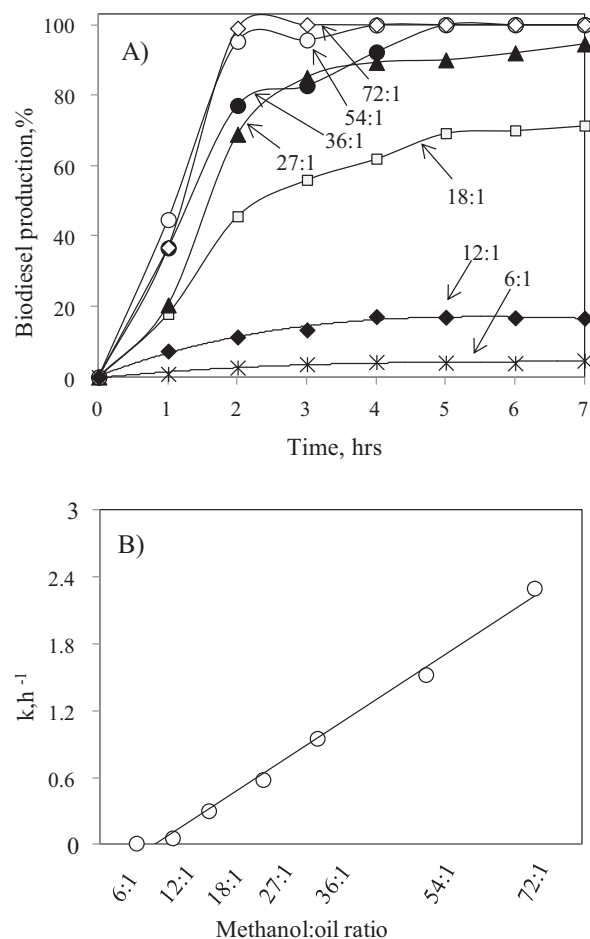


Fig. 6. Effect of the methanol to oil molar ratio on the conversion of biodiesel using the 20%K/TiHT catalyst. (A) The methanol to oil ratios used were: 6:1 (X), 12:1 (◆), 18:1 (□), 27:1 (▲), 36:1 (●), 54:1 (○), and 72:1 (◇). (B) Constant rates after 3 h of reaction. The reaction was carried out in contact with air.

carried out with water at 15 °C. Fig. 7 shows that the rate of methyl ester production is very low at room temperature, but when the temperature is increased to 40 °C the conversion to methyl esters considerably increases. Raising the reaction temperature to 55 °C led to a complete conversion to methyl esters after 5 h of reaction. Further increasing the reaction temperature to 65 °C resulted in a similar rate to that obtained at 55 °C. Fig. 7B clearly shows a steady increase in the reaction constant of the transesterification reaction with temperature until it levels out around 65 °C. The calculated activation energy was 85 kJ/mol, similar to the energy reported by Zhang et al. [41] (79.1 kJ/mol) when using a solvent free KOH catalyst in the transesterification of palm oil.

3.6.4. Reusability of the 20%K/TiHT catalyst

Since the aging process of the catalyst under practical applications is of great interest, several successive runs were carried out with the 20%K/TiHT catalyst. The reaction conditions were the same as before with a catalyst loading of 6% (w/w), oil to methanol molar ratio of 1:36, and temperature of reaction of 65 °C. Similar to reported literature [7,18,22,23], the total number of consecutive runs to study the reusability of the catalyst was selected as four. For this purpose, the same solid catalyst was recovered after each reaction cycle, washed with ethanol, dried overnight at 100 °C, and ex situ calcined at 500 °C before the next reaction step. The latter reactivation procedure was carried out to ensure a proper elimination of possible remaining organics from the surface of the catalysts. Not including the calcination step led to conversions lower than 10%.

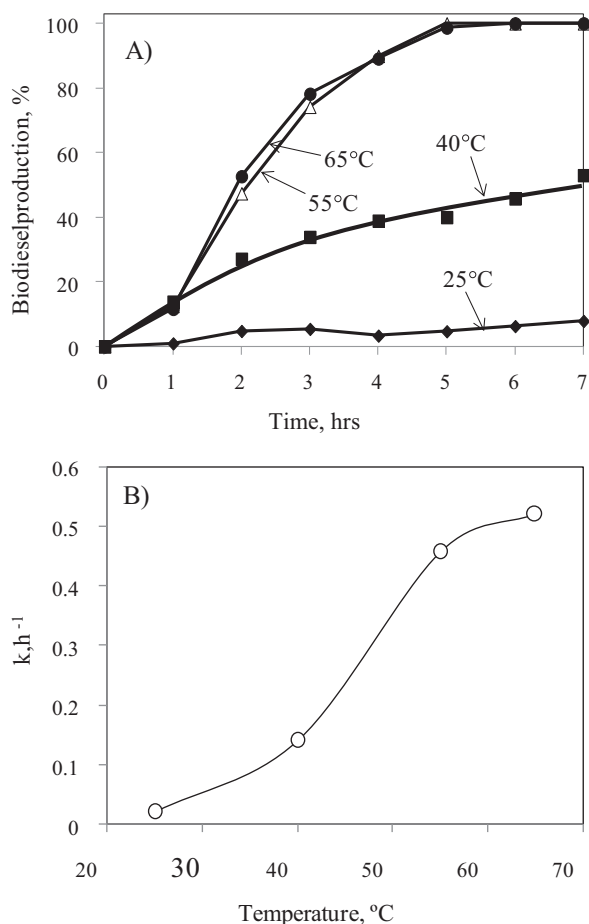


Fig. 7. Transesterification reaction carried out at different temperatures: 25 °C, 40 °C, 55 °C, and 65 °C on the 20%K/TiHT catalyst. (A) Conversion to methyl esters over time and (B) variation of the reaction constant with the reaction temperature after 3 h of reaction. The methanol to oil molar ratio used in all experiments was 36:1. The reaction was carried out in contact with air.

The results presented in Fig. 8 show the four cycles of the reaction. It can be noted that no deactivation of the catalyst or leaching of active species were observed, obtaining an average conversion of $81 \pm 6\%$ after four cycles using the same catalyst.

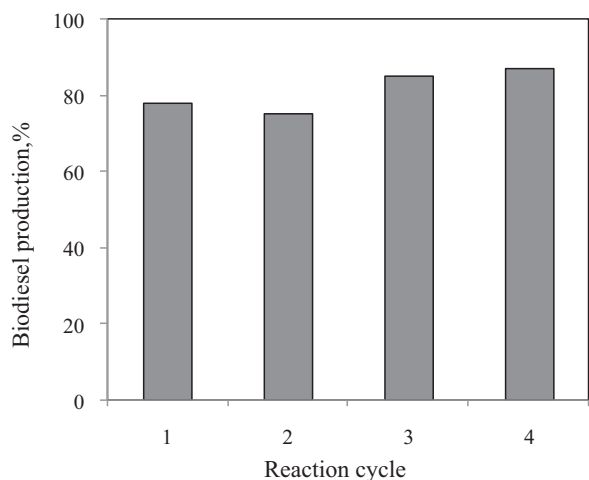


Fig. 8. Transesterification activity after 3 h of reaction with the 20%K/TiHT catalyst calcined at 500 °C. The same catalyst was recovered each time, washed with ethanol, dried at 100 °C, and calcined at 500 °C before the next reaction cycle. The reaction was carried out in contact with air.

4. Discussion

Overall, the results showed that the higher the calcination temperature the higher the conversion achieved with the K/TiHT catalysts. The increasing temperature led to the crystallization of the catalyst into a new phase. The transition from anatase to a titanate phase, where K and Ti are in close interaction, demonstrated more activity in the transesterification reaction. A similar behavior has been reported for potassium and aluminum in the same reaction, where both metals show the formation of an Al–O–K compound when calcined at high temperatures [4,6,8–11,18]. Whereas some studies have found that activity increases with the presence of Al–O–K species [4,10,11], other reports observe the opposite effect [8,18]. Boz et al. [4], attributed higher activity of the Al–O–K species to higher basicity provided by these species. On the contrary, Soetaredjo et al. [18] assigned lower basicity to the Al–O–K species when compared with K₂O. They argue that higher loadings of potassium would favor the formation of Al–O–K species with the detriment of the most active K₂O species. Similarly, Xie et al. [8], found that using a high loading of potassium and a high calcination temperature resulted in the formation of a spinel compound containing Al and K elements, which would be associated with the disappearance of K₂O and, therefore, lower activity. On the other hand Benjapornkulaphong et al. [10], attributed higher activity to the dilution of the potassium aluminate in the aqueous phase of the reacting solution, which would result in the most active homogeneous transesterification reaction. A higher activity was also observed by Ma et al. [11], but they attributed the higher activity of surface KAlO₂ species to the formation of an oxygen layer with higher electron donation ability. The discrepancy in the results found in the literature and exemplified in the alumina supported potassium catalysts might be a result of different reaction conditions since it is well known that multiple variables affect the transesterification reaction (some are presented in the present study). The point that should be kept in mind is that the actual resulting catalyst structure determines the final activity. In the case presented in this study, calcination at high temperatures is able to transform the supported catalysts into a titanate form of oxide. It is possible that the presence of K–O–Ti species, where the metals are in close interaction, results in a more active layer of surface sites, which in turn leads to higher methyl ester conversions. On the other hand, when the catalyst is calcined at lower temperatures (below 600 °C) one can see the appearance of the K₂O phase. In several studies, the latter species has been ascribed to playing an important role as being part of the active sites on the transesterification reaction [4,6,8–10,18,23]. Therefore, the reported literature and the results presented here indicate that not only the type of alkaline oxide plays a role in the activity, but also the crystalline structure of the catalyst resulting from high temperature calcinations can determine the type of active sites and their level of activity. It is expected that during the formation of the alkaline methoxide the adsorbing methanol interacts differently depending on if the adsorption site is a K₂O site or a K–O–Ti site. Although the data is not conclusive on this point, given the results, we can speculate that the K–O–Ti is much more active. In fact, one should note that the catalysts calcined at high temperatures have a much lower BET area. For example, the BET areas of the catalysts calcined at 300 °C, 500 °C, and 700 °C were 18, 19, and 2 m²/g, respectively. Given the rather low surface area of the most active catalyst, calcined at 700 °C, one would expect much more active sites from that catalyst. The latter result suggests the existence of K–O–Ti sites of much higher activity, which result from calcining the catalyst at high temperatures and obtaining a titanate form of oxide. Even though conclusive proofs are needed, we speculate that the activity of the active Ti–O–K sites increases with the calcination

temperature possibly due to the consolidation of the potassium titanate structure.

For potassium based catalysts, it has been reported that leaching of the alkali phase can occur during the reaction [5]. The latter constitutes a problem since the presence of potassium in the reacting solution would favor the homogeneous route of the transesterification reaction. When using a potassium-supported activated carbon catalyst, Baroutian et al. observed that after consecutive uses the conversion gradually decreased. The same effect was observed when using either a batch reactor [21] or a continuous reactor [22]. This decrease in activity was attributed to the leaching of active sites into the reaction media. Similarly, Soetaredjo et al. [18] only obtained 85% conversion in the third reaction cycle, ascribing this deactivation to accumulated poisoning of active sites during the reaction. Samart et al. [23], were able to partially limit the extension of the deactivation (60% conversion to methyl esters) by using vacuum filtration in between consecutive reactions instead of washing the used catalyst with a methanol–ammonia solution, which gave poorer activity (44% conversion to methyl esters). Xu et al. [20] observed a 30% decrease in activity, but was able to recover it by reloading the potassium precursor on the spent catalyst, although leaching of potassium during the reaction was not reported. Similarly, Boz et al. [4] observed a 38% decrease in activity after the first run. In all, their results point to a lack of chemical stability in the supported potassium phase, which leaches into the organic phase during the reaction conditions. In the same way, several other studies show chemical instability of the supported potassium phase which leaches during further reaction conditions [5–7,10,12,13,17]. This lack of chemical stability leads to lower reaction rates when the same catalyst is reused in successive runs.

We conducted an ICP analysis of the liquid products (methyl esters) after 7 h of reaction. The analysis of the aqueous phase did not show the presence of either K or Ti. These analyses showed small amounts of Ti but increased amounts of K in catalysts calcined at higher temperatures. The amount of K in the liquid products for the catalyst calcined at 300 °C, 500 °C, and 700 °C was 24 ppm, 68 ppm, and 137 ppm, respectively. This presence of potassium in the liquid product is a problem since it suggests that the homogeneous reaction is taking place. The latter can be ascribed to the dissolution of potassium by methanol: $\text{KTiO}_2 + \text{CH}_3\text{OH} \rightarrow \text{TiOOH} + \text{K}^+ + \text{CH}_3\text{O}^-$ in which the dissolved CH_3O^- species is responsible for the occurrence of the homogeneous reaction [5]. Since it was unclear to what extent the leaching of potassium was contributing to the reaction, the following experiment was designed to clarify this point. Each one of the calcined catalyst was refluxed and stirred separately in methanol (no reaction) for 7 h and then filtrated (forced leaching). The amount of recovered methanol in these three separate solutions was the same methanol required to conduct the transesterification reaction in the same conditions used during the heterogeneous transesterification reaction, but this time the three separate methanol solutions contained 24 ppm, 68 ppm, and 137 ppm of potassium (forced leaching). These three solutions were used to carry out the reaction. In other words, the reactions were conducted only with the methanol containing the forced leached potassium species and in the absence of a solid catalyst. Using these separate solutions after 7 h of reaction, the conversion to methyl esters resulted in 1%, 6%, and 27% in the solutions (forced leaching) containing 24 ppm, 68 ppm, and 137 ppm of K, respectively. Based on this result, one can prematurely conclude that part of the leached potassium actually contributes to the overall conversion. However, one must consider that after refluxing the catalyst with methanol, the recovered liquid was then centrifuged at only 6000 rpm and colloidal potassium oxide could have remained suspended in the transparent recovered methanol solution. In this case the reaction would still be occurring under

heterogeneous conditions with no ionic potassium contribution. In order to elucidate the latter point, three methanol solutions were prepared containing 24 ppm, 68 ppm, and 137 ppm of ionic potassium using potassium hydroxide as a precursor. Using these solutions the homogeneous transesterification reaction was again carried out in the absence of a solid catalyst. After 7 h of reaction the conversion to methyl esters resulted in 3%, 54%, and 65% for the solutions containing 24 ppm, 68 ppm, and 137 ppm of ionic potassium, respectively. Consequently and as expected, the presence of ionic potassium led to much higher activity levels, which in turn indicate that the potassium leached into the methanol solution under heterogeneous reaction conditions and therefore is an oxide form of potassium. It is possible that these leached potassium and titanium species detected by ICP after reaction remained as suspended colloids even after centrifuging the solution. Whether the potassium oxide leached into the reaction solution is a crystalline or amorphous form of potassium is not clear at this point and is currently being studied. Nevertheless, it can be concluded that the transesterification reaction mainly occurs under heterogeneous conditions. Moreover, the potassium phase seems to be much more resistant when supported by a hydrothermally treated TiO_2 since it shows stable conversion during successive runs. In summary, the results prove that the hydrotreated TiO_2 supported potassium catalyst shows good stability and high conversion of canola oil to biodiesel. Even though CO_2 adsorbs on these catalysts after exposing them to air, they are able to show high activity during successive runs. This important result makes these catalysts very interesting for practical applications since no special pre-treatment of the catalyst is needed, which in turn can lower the operational costs. In a previous work using TPD experiments [25], we observed an important CO_2 desorption at low temperature (<90 °). This desorption of carbonates might be occurring also under reaction conditions, which would explain the activity of all catalysts exposed to air.

5. Conclusions

TiO_2 supported potassium catalysts (K/TiHT) were studied and applied to the transesterification of canola oil into biodiesel. The catalysts proved to be highly stable upon successive runs of spent catalysts. Although colloidal catalyst was present in the final product, it was found that the presence of cationic potassium was negligible in the reaction media. Therefore, the reaction mostly occurred in heterogeneous conditions.

Several variables of reaction were studied and it was found that the optimum catalyst loading into the reaction media was 6% (w/w). It was also found that increasing the methanol to oil ratio steadily increased the conversion to methyl esters. A ratio of 54:1 gave the highest conversion. Also, increasing the reaction temperature up to 55 °C led to the highest level of activity. Higher calcination temperatures of the catalysts resulted in higher conversions, reaching a maximum above 600 °C. It was similarly found that the latter calcination temperature led to the formation of a highly active titanate form of oxide.

The promising results presented here show that the materials studied have interesting activity levels and are highly robust when subjected to successive runs especially since in situ pretreatment of the catalysts and inert reaction environments were not needed.

Acknowledgment

The fellowship AT-24100012 from the National Commission for Science and Technology of Chile (CONOCYT) is gratefully acknowledged.

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